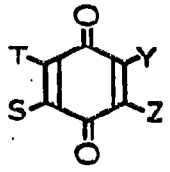
Thin-layer chromatography of simple naturally occurring benzoquinones

Simple alkyl and alkoxyl benzoquinones, as shown in Fig. 1 and Table I, have been found to occur naturally in fungi, higher plants and arthropods[1,2]. The biosynthesis of fungal benzoquinones has been extensively studied, mainly by PETTERSSON[3], while the biosyntheis of these derivatives from plants and arthropods is a continuing problem in this department.



(I)	Y=Z=S=T=H	(IX)	Y=T=OCH_3; Z=S=H
(II)	Y=CH_3; Z=S=T=H	(X)	Y=CH_3; Z=T=H; S=$CH(CH_3)_2$
(III)	Y=C_2H_5; Z=S=T=H	(XI)	Y=CH_2OH; Z=S=T=H
(IV)	Y=CH_3; Z=OCH_3; S=T=H	(XII)	Y=S=OCH_3; Z=T=H
(V)	Y=OCH_3; Z=S=T=H	(XIII)	Y=Z=CH_3; S=T=OCH_3
(VI)	Y=Z=CH_3; S=T=H	(XIV)	Y=CH_3; Z=H; S=OCH_3; T=OH
(VII)	Y=S=CH_3; Z=T=H	(XV)	Y=CH_3; Z=T=OH; S=OCH_3
(VIII)	Y=Z=S=CH_3; T=H	(XVI)	Y=CH_3; S=OCH_3; Z=T=H

Fig. 1. Naturally occurring alkyl and alkoxyl benzoquinones.

TABLE I

NATURALLY OCCURRING ALKYL AND ALKOXYL BENZOQUINONES

Compound	*Formula*	*Source*	*Authority*
Benzoquinone	(I)	Various arthropods	4
Toluquinone	(II)	Various arthropods	4
2-Ethylbenzoquinone	(III)	Various insects	4
2-Methyl-3-methoxybenzoquinone	(IV)	Various diplopods	4
2-Methoxybenzoquinone	(V)	Wheat germ	5
		Tribolium castaneum	6
2,3-Dimethylbenzoquinone	(VI)	*Heteropachyloidellus robustus*	7
2,5-Dimethylbenzoquinone	(VII)	*Heteropachyloidellus robustus*	7
2,3,5-Trimethylbenzoquinone	(VIII)	*Heteropachyloidellus robustus*	7
2,6-Dimethoxybenzoquinone	(IX)	Wheat germ	8
		Adonis vernalis	9
		Several species of *Simarouba* and *Meliacae*	10
Thymoquinone	(X)	*Tetraclinis articulata*	11
		Libocedrus decurrens	12
Gentisylquinone	(XI)	*Penicillium patulum*	13
		Penicillium divergens	14
2,5-Dimethoxybenzoquinone	(XII)	*Polyporus fumosus*	15
Aurantiogliocladin	(XIII)	*Gliocladium* species	3
Fumigatin	(XIV)	*Aspergillus fumigatus*	3
Spinulosin	(XV)	*Aspergillus fumigatus*	3
		Penicillium species	3
Coprinin	(XVI)	*Coprinus similis*	3
		Lentinus degener	3

Benzoquinones have been the most widely found components of arthropod defensive substances having been isolated from at least six orders belonging to the classes, Insecta, Diplopoda and Arachnida[4]. To date, the benzoquinones which have been identified as defensive agents are compounds (I) to (VIII).

Since our attention is directed particularly towards the identification and mode of biosynthesis of the arthropod benzoquinones, it was considered desirable to utilise thin-layer chromatography as a method of isolation, separation and possible identification of these compounds which are obtained from the animals in minute quantities.

We now wish to report the data given in Table II for ten of the compounds listed above.

TABLE II

R_F VALUES × 100 OF SIMPLE NATURALLY OCCURRING QUINONES

Chromatography was carried out at the constant temperature of 24.5°, using the same amount of material in each case and allowing the solvent to move a distance of 15 cm.

Compound	*Absorbent*[a]	*X*				*Y*				*Z*			
	Eluting solvent[b]	*A*	*B*	*C*	*D*	*A*	*B*	*C*	*D*	*A*	*B*	*C*	*D*
(I)		65	70	60	60	40	55	50	45	80	80	70	75
(IX)		20	55	25	35	10	30	15	15	40	70	40	60
(V)		35	60	30	50	15	40	30	30	65	75	70	65
(II)		55	70	70	60	25	55	45	45	75	80	75	80
(X)		65	75	75	70	60	70	60	55	85	85	85	90
(VI)		55	70	75	65	44	65	45	40	80	85	75	85
(VII)		60	70	70	60	45	60	50	45	80	90	75	75
(VIII)		60	70	70	65	55	65	55	60	80	85	85	90
(IV)		65	60	85	60	50	35	25	35	85	85	75	85
(XI)		10	15	15	20	5	10	5	5	15	5	10	10

[a] X = Eastman Chromogram K301 R; Y = Kieselgel GF_{254}; Z = Alumina G.
[b] A = Benzene–methanol–acetic acid (40:1:1); B = chloroform; C = chloroform–xylene (3:1); D = chloroform–benzene (3:1).

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